Indian J. Phys. **78(12)**, 1381-1384 (2004)

AN INTERNATIONAL JOURNAL
IJP

Spectral and normal coordinate analysis on the molecule of bis(thiourea) cadmium chloride single crystal

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Received 27 December 2003, accepted 22 July 2004

Abstract : Single crystals of bis(thiourea) cadmium chloride (BTCC) have been grown from saturated aqueous solution by slow evaporation method at room temperature. FTIR and FT Raman spectra have been recorded. The normal coordinate analysis has been carried out with an orthonormal set of symmetry coordinates following Wilson F-G matrix method. The potential energy distribution has also been evaluated.

Keywords : Normal coordinate analysis, FTIR spectra, FT Raman, force constants.

PACS Nos. : 81.10.-h, 33.20.Ea, 33.20.Fb

1. Introduction

Nonlinear optical (NLO) materials find applications in the areas of laser technology, optical communication and data storage technology. Semiorganic crystal which have the combined properties of both inorganic and organic crystal, are of current interest. Among the semiorganic nonlinear optical materials, metal complexes of thiourea which have low UV cut off wavelengths, applicable for high power frequency conversion, have received much attention. These materials can be used as better alternatives for KDP crystals in frequency doubling and laser fusion experiments due to their higher values of laser damage threshold. Bis(thiourea) cadmium chloride (BTCC) is one such efficient semi-organic nonlinear material which is used for second harmonic generation (SHG) [1–4]. BTCC is 110 times more nonlinear than quartz [5]. Xing *et al* [4] have reported BTCC as an efficient semiorganic nonlinear optical material for SHG. Venkataramanan *et al* [6] have reported that the BTCC crystals have the highest laser induced damage threshold values among the other solution-grown NLO crystals. BTCC belongs to the orthorhombic crystal class with the space group $Pmn2_1$. The lattice parameters are a = 13.147 Å, b = 5.843 Å and c = 6.518 Å. In the present work, FTIR and FT Raman spectral measurements have been carried out, to make an investigation on the molecular structure of BTCC crystal.

2. Experimental details

BTCC salt was synthesized using analar grade cadmium chloride and thiourea in deionised water in a stoichiometric ratio 1 : 2 . The required quantity of cadmium chloride and thiourea were estimated from the following reactions :

$$CdCl_2 + 2[CS(NH_2)_2] \rightarrow Cd[CS(NH_2)_2]_2.Cl_2.$$

The calculated amount of the salts was dissolved in the deionised water. This solution was heated and left for evaporation to dryness at room temperature. The purity of the synthesized salt was increased by successive recrystallization process. Temperature as low as 45°C was maintained in order to avoid decomposition. Good quality seeds obtained by slow evaporation were used for the growth. Transparent crystals of dimension upto 18 × 7 × 3 mm^3 were grown in about six weeks.

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The Fourier transform infrared (FTIR) spectrum of BTCC crystals were recorded in range 4000–400 cm^{-1} and 500–50 cm^{-1} employing a BRUKER IFS 66v model FTIR spectrometer using KBr and polyethylene pellets respectively. The FT Raman spectrum of the crystal has been recorded in the range 4000–100 cm^{-1} using BRUKER IFS 66v model FTIR spectrometer – FRA Raman module with YAG laser.

3. Molecular structure and symmetry considerations

The molecular structure of BTCC crystal [7] and its FTIR and FT Raman spectra are shown in Figures 1, 2 and 3 respectively. The crystal structure consists of two molecular units in a unit cell. In the coordination polyhedron, cadmium is coordinated to two sulphur's from two thiourea molecules and to two chlorine atoms, to form a tetrahedral arrangements. The molecule is assumed to have C_{2v} point group symmetry by treating

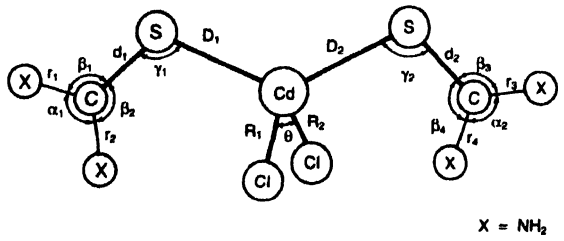

Figure 1. Molecular structure of BTCC.

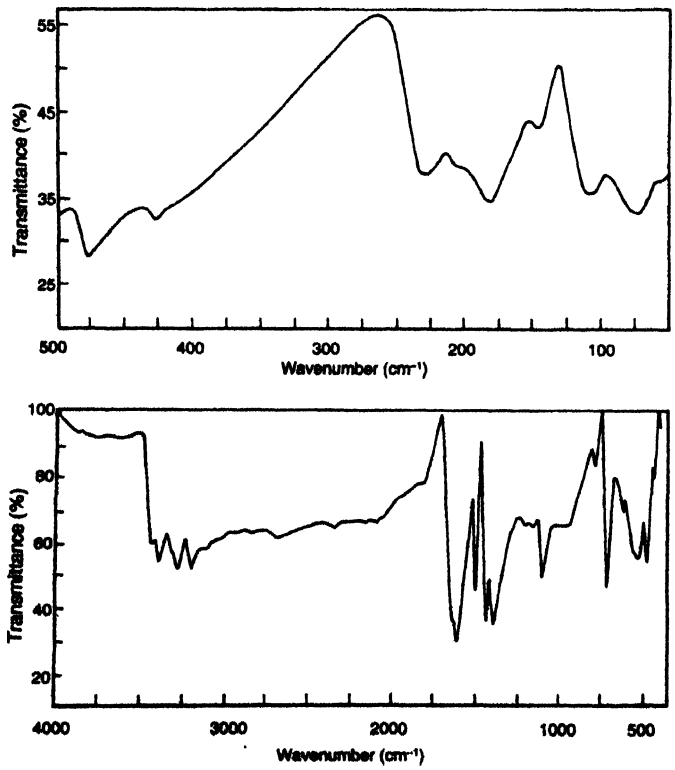

Figure 2. FTIR spectrum of BTCC.

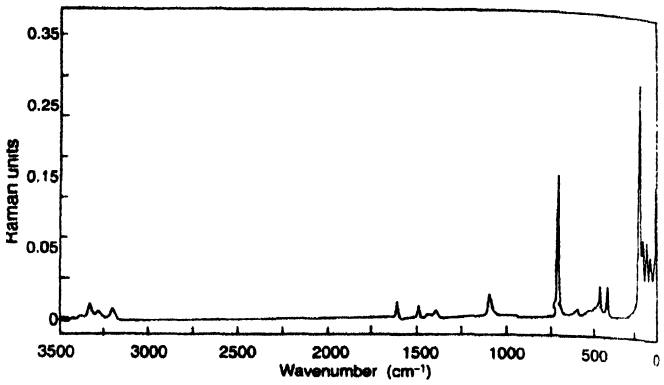

Figure 3. FT Raman spectrum of BTCC.

the NH_2 group as point mass. BTCC has 27 fundamental normal modes of vibration under C_{2v} symmetry point group and are distributed as

$$\Gamma_{vib} = 9A_1(IR,R) + 5A_2(R) + 6B_1(IR,R) + 7B_2(IR,R).$$

All the modes are Raman active. Except A_2, other modes are infrared active. The present set of symmetry coordinates are more than sufficient for structural elucidation, and hence some of the 19 specific modes of vibrations are considered for normal coordinate analysis. A systematic set of symmetry coordinates has been arrived at, using the knowledge of projection operator and the character table pertaining to the C_{2v} symmetry point group. The symmetry coordinates thus obtained, are as follows :

A_1 species :

$$S_1 = 1/\sqrt{2}[\Delta D_1 + \Delta D_2],$$

$$S_2 = 1/\sqrt{2}[\Delta R_1 + \Delta R_2],$$

$$S_3 = 1/\sqrt{2}[\Delta d_1 + \Delta d_2],$$

$$S_4 = 1/2[\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4],$$

$$S_5 = [\Delta\theta],$$

$$S_6 = 1/\sqrt{2}[\Delta\alpha_1 + \Delta\alpha_2],$$

$$S_7 = 1/2[\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4].$$

A_2 Species :

$$S_8 = 1/\sqrt{2}[\Delta D_1 - \Delta D_2],$$

$$S_9 = 1/\sqrt{2}[\Delta d_1 - \Delta d_2],$$

$$S_{10} = 1/\sqrt{2}[\Delta\gamma_1 + \Delta\gamma_2].$$

B_1 Species :

$$S_{11} = 1/\sqrt{2}[\Delta R_1 - \Delta R_2],$$

$$S_{12} = 1/2[\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4],$$

$$S_{13} = 1/\sqrt{2}[\Delta\alpha_1 - \Delta\alpha_2],$$

$$S_{14} = 1/2[\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4].$$

B_2 Species :

$$S_{15} = 1/2\ [\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4],$$

$$S_{16} = 1/2\ [\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4],$$

$$S_{17} = 1/\sqrt{2}[\Delta\gamma_1 - \Delta\gamma_2],$$

$$S_{18} = 1/2\ [\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4],$$

$$S_{19} = 1/2\ [\Delta\beta_1 + \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4].$$

where Δ's represent changes in the corresponding bond distances and bond angles. The required structural data were taken from literature [7].

4. Normal coordinate analysis

A normal coordinate analysis for BTCC has been carried out using the observed frequencies from the FTIR and FT Raman spectra. The evaluation of force constants are made on the basis of general valence force field by applying wilosn's *F-G* matrix method [8–10]. The correctness of the assignment is verified by evaluating the potential energy distribution (PED) using the relation PED-$F_{ik}L^2_{ik}/\lambda_k$, where PED is the contribution of the i-th symmetry coordinate to the potential energy of vibration whose frequency is ν_k. The observed frequencies along with the assignments, calculated force constants and the percentage of potential energy distribution for BTCC are presented in Table 1. The initial set of force canstants for the BTCC has been taken from the related molecules [11]. This set of force constants were subsequently refined by keeping a few interaction constants fixed throughout the refinement process.

4.1. Vibrational assignments :

The high wave number region lying in between 3400–3100 cm^{-1} arises due to the N–H stretching vibrations [12]. The absorption bands observed at 3198 cm^{-1} and 3388 cm^{-1} in the FTIR spectrum, have been assigned to NH_2 symmetric and asymmetric stretching vibrations respectively. In the FT Raman spectrum, these bands appear at 3205 cm^{-1} and 3374 cm^{-1}. The NH_2 bending vibrational line is observed as very strong at 1620 cm^{-1} in FTIR spectrum but this vibrational line is observed at 1619 cm^{-1} in Raman spectrum. The bands at 1096 cm^{-1} and 1493 cm^{-1} in FTIR spectrum are attributed to the C–N symmetric and asymmetric stretching vibrations respectively. In FT Raman spectrum, these bands appear at 1103 cm^{-1} and 1500 cm^{-1}. The strong absorption bands observed at 714 cm^{-1} and 1389 cm^{-1} in the FTIR spectrum can be assigned to the C=S symmetric and asymmetric stretching vibrations [13]. In the FT Raman spectrum, the corresponding bands appear at 720 cm^{-1} and 1399 cm^{-1}. The very weak bands at 500 cm^{-1} and 541 cm^{-1} in the FT Raman spectrum are due to C–S–Cd bendings. The symmetric and asymmetric bending vibrations of N–C–S appear at 476 cm^{-1} and 610 cm^{-1} respectively in the FTIR spectrum. The bands observed at 427 cm^{-1} and 528 cm^{-1} in FTIR spectrum are attributed to N-C-N symmetric and asymmetric bending vibrations respectively. The N–C–N symmetric bending vibration appeared at 430 cm^{-1} in the FT Raman spectrum.

The low frequency range of the spectra consists of bands which are due to the Cd–Cl and Cd–S vibrations [14]. The metal halogen vibrations of thiourea complexes have been investigated by several researchers [15,16]. The bands observed at 146 cm^{-1} and 182 cm^{-1} in the FTIR spectrum, have been assigned to Cd–Cl symmetric and asymmetric stretching respectively. In FT Raman spectrum, these bands appear at 146 cm^{-1} and 172 cm^{-1}. The bands observed at 203 cm^{-1} and 224 cm^{-1} in the FT

Table 1. Vibrational assignment, force constant (10^2 N/m) and PED values of BTCC.

Symmetry coordinate constant	Frequency (cm^{-1}) FTIR	Raman	Assignment	Symmetrised Force	PED %
A_1 species					
ν_1	146	146	Cd–Cl sym. stretching	0.3566	85
ν_2	210	203	Cd–S sym. stretching	0.4647	90
ν_3	714	720	C–S sym. stretching	5.8721	72
ν_4	1096	1103	C–N sym. stretching	6.4644	92
ν_5	106	106	Cl–Cd–Cl sym. bending	0.2262	65
ν_6	427	430	N–C–N sym. bending	1.1672	78
ν_7	476	476	N–C–S sym. bending	0.6173	62
A_2 species					
ν_8	-	224	Cd–S asym. stretching	0.5843	80
ν_9	-	1399	C–S asym. stretching	8.2491	90
ν_{10}	-	500	C–S–Cd sym. bending	0.6324	74
B_1 species					
ν_{11}	182	172	Cd–Cl asym. stretching	0.4457	100
ν_{12}	1493	1500	C–N asym. stretching	8.5264	95
ν_{13}	528	-	N–C–N asym. bending	1.3549	85
ν_{14}	610	608	N–C–S asym. bneding	0.8124	82
B_2 species					
ν_{15}	1437	1433	C–N asym. stretching	8.3243	90
ν_{16}	1493	1500	C–N asym. stretching	8.5264	93
ν_{17}	-	541	C–S–Cd asym. bending	0.7281	79
ν_{18}	610	608	N–C–S asym. bending	0.8124	80
ν_{19}	775	-	N–C–S asym. bending	0.9824	66

Raman spectrum have been attributed to Cd–S symmetric and asymmetric stretching respectively.

5. Conclusions

BTCC single crystals have been grown by slow evaporation technique at room temperature. A satisfactory vibrational band assignment of BTCC has been successfully carried out using FTIR and FT Raman spectral measurements. The symmetrised force constants for the various symmetry coordinates are calculated. To check whether the chosen set of assignments contribute maximum to the potential energy associated with normal coordinates of the molecule, the potential energy distribution (PED) has been calculated.

Acknowledgment

One of the authors (VJ) is thankful to the University Grants Commission, Government of India, for the award of a teacher fellowship.

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